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Effect of rapid thermal annealing: red and blue shift in photoluminescence of GaNAs grown by RF plasma-assisted molecular beam epitaxy

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ABSTRACT

Rapid thermal annealing (RTA) of 1000Å GaNAs films grown on (100) oriented GaAs substrate by radio frequency (RF) plasma assisted solid-source molecular beam epitaxy was studied by low-temperature photoluminescence (PL) and high-resolution x-ray diffraction (HRXRD). Samples with nitrogen content of 1.3 and 2.2% have shown an overall blueshift in energy of 67.7meV and an intermediate redshift of 42.2meV in the PL spectra when subjected to RTA at 525-850°C for 10min. It is also shown that the sample, which is annealed at temperature range of 700-750°C, has the highest photoluminescence efficiency (1.7-2.1 times increase in integrated PL intensity as compared to the as-grown sample). Reciprocal space mapping of the as-grown GaNAs samples obtained by using triple-crystal HRXRD shows the presence of interstitially incorporated of N atoms with no lattice relaxation in the direction parallel to the growth surface. These results have significant implication on the growth and post-growth treatment of nitride compound semiconductor materials for high performance optoelectronics devices.

INTRODUCTION

Group III-N-As is a promising material for 1.3 and 1.55µm telecommunication optoelectronic devices grown on GaAs substrate. Hence, epitaxial growth of the nitride compound has been studied extensively. It is known that the luminescence efficiency of these alloys can be greatly improved by annealing at temperature higher than the growth temperature [1]. The same has been reported for quantum well structures of GaNAs/GaAs [2]. However, along with large improvement in the PL efficiency, a significant blueshift (9-50meV) of the maximum PL intensity position was also observed which seemed independent of the N composition. This blueshift effect in the PL peak energy has been attributed mainly to two possible reasons; (i) nitrogen out-diffusion from bulk GaNAs [3], and (ii) interdiffusion of N-As atoms near the interface of GaNAs/GaAs [4,5]. However, the results from our experiments suggest the presence of a different mechanism of diffusion. This is shown by an intermediate redshift in the PL peak energy in annealing temperature range lower than the optimum temperature. Furthermore, such changes were not accompanied by a shift towards higher Bragg angle for the GaNAs peak in HRXRD, a result different from others [6,7].

EXPERIMENTAL DETAILS

All our samples were grown by solid-source molecular beam epitaxy (SSMBE) with nominal structures of 200Å GaAs/1000Å GaNAs/3000Å GaAs buffer layer on semi-insulating GaAs (100) substrate using elemental sources of gallium (7N), arsenic (6N) and a nitrogen radio-frequency (RF) plasma source. Prior to growth of GaNAs, oxide desorption was carried out at 580°C under As overpressure, following which 300nm of GaAs buffer layer was grown. The As/Ga flux ratio was fixed at ~20 and the growth rate of GaAs at 1µm/hour. Since only a small amount of nitrogen is to be incorporated into the nitride layer, we expect no significant change in the GaNAs growth rate under the same Ga flux. A growth interruption of ~5min was used to stabilize the ignition of the nitrogen RF plasma source with N₂ background pressure of 1.0×10^{-5} Torr (at 0.10 sccm of N₂ flow). The GaNAs layer was grown at 500°C and clear (2×4) surface reconstruction was observed. GaNAs samples with different nitrogen composition were prepared by varying the RF power from 150-250W. This was followed by rapid thermal annealing (RTA) of the samples at 525-850°C for 10min under N₂ ambient. During the RTA process, the samples were capped using a GaAs wafer to minimize arsenic loss at elevated temperature. Low-temperature photoluminescence (PL) at 10K was excited by a 514.5nm ion argon laser and detected using a liquid nitrogen cooled Ge detector in conjunction with standard lock-in technique. The samples were also characterized by high-resolution x-ray diffraction (HR-XRD) for their crystalline quality (rocking curve and triple-axis scan) and the nitrogen content was determined by fitting the experimental x-ray rocking curve with the simulated rocking curve using dynamical diffraction theory.

DISCUSSION

During the growth of GaNAs at low substrate temperature of 500°C, the nitrogen atoms are incorporated into the nitride-arsenide matrix not only by substituting the As lattice site but also as interstitial nitrogen complex and/or molecular nitrogen in GaNAs. In our experiment, a (2×4) surface reconstruction was observed throughout the growth of the GaNAs layer. Since the nitrogen atom and N₂ molecule are smaller compared to the radius of the interstitial site, it is relatively easy for nitrogen to be incorporated into the interstitial site of the host lattice. As reported by Spruytte *et. al.* [7], nitrogen can exist in two configurations in the GaNAs layer grown using a RF plasma nitrogen source; (i) by forming a covalent Ga-N bond (a substitutional β site: replacing As host sublattices with N atoms), an effect which primarily contributes to the band gap narrowing (redshift) due to the highly localized nature of the perturbation introduced by nitrogen atoms [8], (ii) by forming a nitrogen complex in which nitrogen is less strongly bonded to Ga atoms (an interstitial site).

The change in PL peak energy, full-width at half maximum (FWHM) and PL integrated intensity for samples with N contents of 1.3% and 2.2%, respectively, with annealing temperature from 525-850°C is shown in Fig. 1(a)-(b).

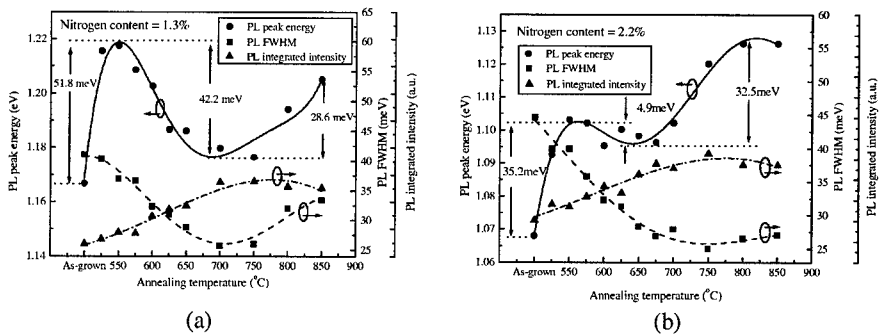


Figure 1(a)-(b). Plot of PL peak energy, integrated intensity and FWHM at different annealing temperature for samples with N content of (a) 1.3% and (b) 2.2%

Fitted lines are drawn to show the changes in these parameters following the change of annealing temperature. The thermal annealing caused an initial blue, and intermediate redshift shift in the PL peak energy, and could not be explained solely by the effect of nitrogen out-diffusion [7], or N-As atom interdiffusion across the GaNAs/GaAs heterointerface [4,5]. Because the amount of nitrogen incorporation into the GaAs lattice is very small, the nitrogen atoms adopt an impurity-like behavior in the lattice [9]. Under such a condition, it is most likely that a substitutional-interstitial diffusion mechanism [10] could take place during the thermal annealing process, which results in hopping of substitutional nitrogen atoms into interstitial sites and vice versa, according to $S \leftrightarrow I + V$, where S, I and V are the substitutional nitrogen, interstitial nitrogen and vacancy, respectively. Depending on the annealing temperature, the blueshift of the PL peak energy could have been caused by hopping of nitrogen atoms from substitutional sites to interstitial sites, or nitrogen out-diffusion, or a mixture of both mechanisms. The intermediate redshift in the PL peak energy could have been caused by a 'kick-out' effect of the substitutional arsenic atoms by interstitial nitrogen atoms.

For the sample with N content of 1.3%, grown at a lower RF plasma power of 150W, an increase in annealing temperature from 525°C to 550°C gave rise to an increase in PL peak energy from 1.166 to 1.218 eV (a total blueshift of 51.8 meV). As the annealing temperature was increased further, the PL peak energy reduces, equivalent to a total redshift of 42.2 meV (from 1.218 to 1.176 eV). The observed initial blueshift in the PL peak energy suggests a condition whereby the lattice is energetically favorable for the substitutional nitrogen atoms to diffuse into nearby interstitial sites. When the annealing temperature is increased further, the observed redshift in the PL peak energy could be due to a condition whereby it is energetically favorable for interstitial nitrogen atoms to replace As atom sites and become substitutional nitrogen atoms. Therefore, under such circumstances, the former will produce a bandgap widening effect and the latter, a bandgap narrowing effect with a change in substitutional atom sites from As to N.

In comparison, the sample with N content of 2.2% grown using higher RF plasma power of 250W, exhibit a similar trend of initial blueshift in the PL peak energy of 35.2 meV when the annealing temperature was increased to 550°C. An intermediate redshift in the PL peak energy of 4.9 meV was observed, but it is ~9 times smaller compared to that in the sample with lower

nitrogen content. The reduction in the PL peak energy reaches a minimum at annealing temperature of $\sim 650^{\circ}\text{C}$, which is lower compared to the sample with lower N content ($\sim 725^{\circ}\text{C}$). Such a difference could arise from the difference in the concentration of interstitially incorporated nitrogen atoms between these two samples. The sample with lower nitrogen content has a higher ratio of interstitial nitrogen atoms to substitutional ones, because when lower RF plasma power was used, a lower ratio of nitrogen atoms to 1st and 2nd positive molecules were generated [11] and hence, a considerable concentration of nitrogen is incorporated into the interstitial sites. Hence, the sample with lower nitrogen content of 1.3% will require higher annealing temperature in order to replace most of the substitutional As by interstitial nitrogen atoms. Therefore, the PL peak energy reaches a minimum value at higher annealing temperature of $\sim 725^{\circ}\text{C}$ compared to that of the sample with higher N content of 2.2%.

The FWHM of the PL peak for both samples showed an approximately common minimum value at annealing temperature of $700\text{--}750^{\circ}\text{C}$ (1.6 and 1.8 times reduction for sample with nitrogen content of 1.3% and 2.2% respectively, as compared to the as-grown condition). This suggests that both samples, regardless of the difference in nitrogen composition, have undergone a similar annihilation of point defects such as interstitials and vacancies in the as-grown GaNAs layer, resulting in improved crystalline quality as shown later in the HR-XRD results. Such defects are detrimental to the photoluminescence efficiency. For both samples, a 1.7-2.1 times increase in the integrated intensity of the PL peak was observed, which reaches a maximum value at annealing temperature of $\sim 770^{\circ}\text{C}$ and appear in close correlation with the respective PL FWHM improvement.

When the annealing temperature was further increased to 850°C for both samples (Fig. 1((a)-(b))), the PL peak energy continued to increase, indicating a normal blueshift in the energy caused primarily by nitrogen out-diffusion. However, such high temperature annealing could cause degradation in the crystalline quality and has a detrimental effect on the optical properties of the material, as evident by the increase in PL FWHM and reduction in the integrated PL intensity.

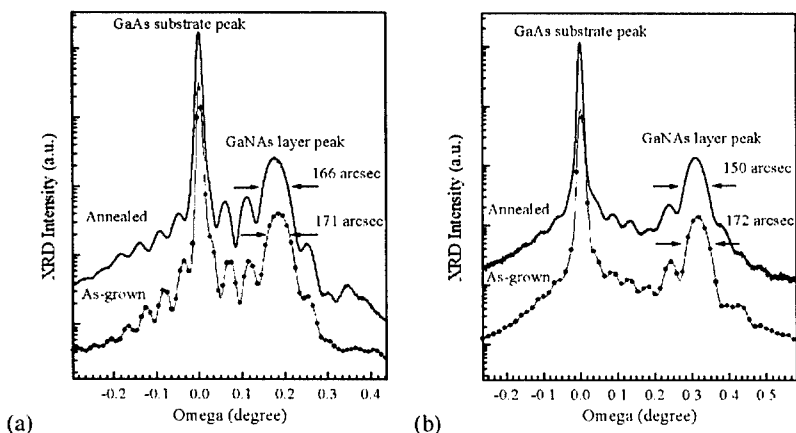


Figure 2(a)-(b). Plot of XRD rocking curves of the as-grown and annealed (750°C for 10min) GaNAs samples with N content of (a) 1.3% and (b) 2.2%

Fig. 2(a)-(b) shows the reduction in FWHM of the XRD peak of the GaNAs layer from 171 to 166 arcsec and from 172 to 150 arcsec for samples with 1.3% and 2.2% nitrogen content, respectively, when annealed at the optimized temperature for best overall optical property of 750°C for 10min (as shown in Fig.1(a)-(b)).

The reduction in FWHM of the XRD peak is consistent with the improved PL efficiency. This is evident from the significant improvement in the PL intensity and corresponding reduction in the PL FWHM. Another noteworthy result is that there are no drastic changes to the position of the XRD peak of the GaNAs layer and the Pendellosung fringes for both samples when subjected to the thermal annealing process. This observation is notably different from that of Spruytte *et al.*³, in which a significant shift of the XRD peak position to lower Bragg angle was recorded indicating significant nitrogen out diffusion when GaNAs (with as-grown N content of 2.5%) was annealed at 760°C for 5min. This shows that in so far as the nitrogen out diffusion from the film is concerned, our samples are more stable, and the effect on the lattice parameter of the GaNAs layer and its interface with GaAs is rather minimal.

Reciprocal space mappings in (004) and (224) reflection points of the as-grown sample with 1.3% N content are shown in Fig 3(a)-(b) below.

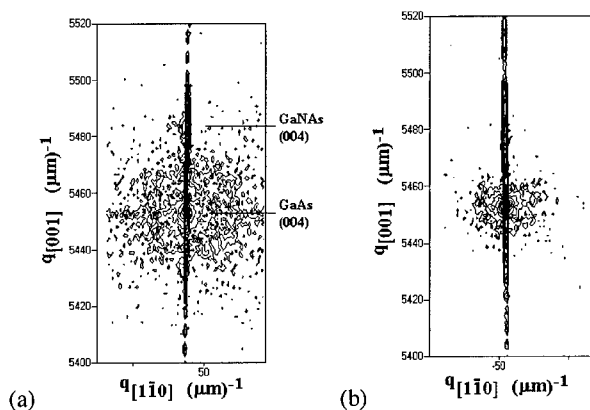


Figure 3(a)-(b). Reciprocal space map in (004) reflection points of as-grown GaNAs with N content of 1.3%, (a) As-grown and (b) Annealed 700°C for 10min.

The kinematical diffuse scattering around the (004) reflection points (Fig. 3(a)) arises from point defects such as interstitials [12]. As expected, these point defects could only be introduced during the growth of GaNAs since some nitrogen atoms are incorporated into interstitial site. When annealed at 700°C for 10min, most of these defects were annihilated as shown by the reduction of kinematical diffuse scattering in Fig 3(b).

CONCLUSION

In summary, we have presented low temperature PL measurements on GaNAs samples with nitrogen content of 1.3% and 2.2%, subjected to rapid thermal annealing from 525-850°C for 10min. The PL peak energy position, which is related to the bandgap of the GaNAs material,

showed significant blueshift and intermediate redshift in energy at annealing temperature lower than the temperature (700-750°C). These effects suggest an intermediate state of diffusion of substitutional-interstitial nitrogen atoms, whereby at certain range of annealing temperature, it is energetically more favorable for interstitial nitrogen atoms to diffuse into substitutional As sites and hence give rise to redshift in the PL peak energy. The minimum PL FWHM and maximum PL integrated intensity were observed to occur approximately at a common annealing temperature of 750°C for both GaNAs samples of different nitrogen content. The XRD results of these samples are consistent with the PL results as evident from a reduction in the FWHM of the XRD peak of the GaNAs layer corresponding to significant improvement in the PL efficiency arising from the thermal annealing process. The results also show no significant difference in the lattice parameter between the annealed and as-grown sample, indicating that the GaNAs layers are structurally more stable under thermal annealing.

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